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A novel water layer structure inside nanobubbles at room temperature*

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Molecularly thin water layer, with a hydrogen bonding network different from those in bulk water and ice, has unique properties and is generally involved in many important processes such as wetting, erosion, atmosphere chemical reaction, protein folding and biomolecular interaction. Here, we report a new water layer structure at room temperature, which is found inside nanobubbles by using synchrotron based scanning transmission soft X-ray microscopy (STXM). The three peaks 535.0, 536.8 and 540.9 eV at O K edge inside the nanobubbles show a novel characteristics of very thin water layers, which has never been observed before.

Keywords: Nanobubble, Soft X-ray absorption, Water layer

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I. INTRODUCTION

Water, a very important substance on the earth, existing in three phases of liquid, vapor and ice, has many odd and peculiar macroscopic properties that have not yet been understood completely in terms of microscopic properties of its constituent water molecules and their mutual interactions. Among various methods developed to reveal the structure of water, the near-edge X-ray absorption fine structure (NEXAFS) spectrum provides information about the local hydrogen bond configurations of water molecules in liquid water, ice and water clusters [1–7].

Water exhibits unique behaviors at an interface. For example, nanoscale gas bubbles were found with spherical cap-shapes attached to a solid surface being immersed in aqueous environment [8–16]. The ambiguous properties of gas nanobubbles remain far from being understood, such as their astonishing stability, which contradicts to classical thermodynamics. According to the Young-Laplace equation, such nanobubbles should not exist at all, since their small radii of curvatures imply so high a Laplace pressure inside the bubbles that they would dissolve almost instantly [17–20]. For micron or nanometer sized bubbles, the classical theory predicts that they should disappear within tens of milliseconds or less. But in the experiments, those interfacial nanobubbles could be there for hours and even days [21].

Water may have a special structure when confined at the interface. Nanobubble offers a nanoscopic confinement for water molecules, and its peculiar behavior may suggest the existence of certain unique water structures inside. However, it is hard to detect the water structure inside the nanobubbles with conventional methods. In this context, zone-plate based scanning transmission soft X-ray microscopy (STXM) has become a unique analysis tool, taking advantages of elemental absorption contrast to image samples down to 15 nm [22]. In principle, the non-intrusive measurement, the nanoscopic spatial resolution and the chemical sensitivity have made STXM an ideal technique to study the properties and behavior of individual nanobubbles at interface.

In this paper, we demonstrate that STXM with nanometer resolution can be used to image nanobubbles between two silicon nitride windows in water solutions. Importantly, it is found that a new type of thin water layers may exist inside nanobubbles according to the O K edge X-ray NEXAFS spectrum.

II. EXPERIMENTAL SECTION

A. Materials

Water with a conductivity of 18.2 MΩ cm was obtained from a Milli-Q system (Millipore Corp., Boston, MA). Silicon nitride (Si_3N_4) windows (5 mm × 5 mm, with 1 mm × 1 mm × 100 nm windows, SN-LDE-510-15, Shanghai NTI Co. Ltd, China) served as the substrates for nanobubbles period.

B. Preparation of nanobubbles

The sample of nanobubbles was prepared as follows. First, millipore water was degassed for about 2 hours at a pressure of 0.1 atm (0.01 MPa) in a desiccator. Then, SF_6 gas (puri-

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ty 99.9999%, from Wonik Materials Co.) was injected into the solutions for about 30 minutes in a washing bottle. One droplet of the gas solution (about 3.0 μL) was deposited onto surface of the Si_3N_4 window, and another Si_3N_4 window was put on top of the droplet gently. Vacuum glue (two components, from Agilent Co.) was used to seal the two Si_3N_4 windows. Usually, the glue curing of about 1.5 h was needed before the sample was loaded into the experimental chamber.

C. STXM imaging

The samples were investigated using the newly constructed BL08U1A STXM microscope at Shanghai Synchrotron Radiation Facility (SSRF) and the SM beamline STXM at Canadian Light Source (CLS). The sample was imaged in a transmission mode in helium ($\geq$ 99.999%, Shanghai Chunyu Special Gas Ltd.) at 0.4–0.66 atm (0.04–0.066 MPa). The transmitted photon flux was measured using a photomultiplier tube (Hamamatsu, Japan). A 800 lines/mm grating and 50 μm exit slit were used for O K edge imaging and spectroscopy, providing an energy resolution of 6000 $(E/\triangle E)$ at 700 eV. Images were recorded at selected energies through the O 1s region (525–550 eV) in 0.2 eV steps. The photon energy was calibrated by measuring pure SF_6 in the experimental chamber at 3–10 Torr (400–1333.2 Pa). The image and spectral processing was carried out using the **aXis** 2000 software [23].

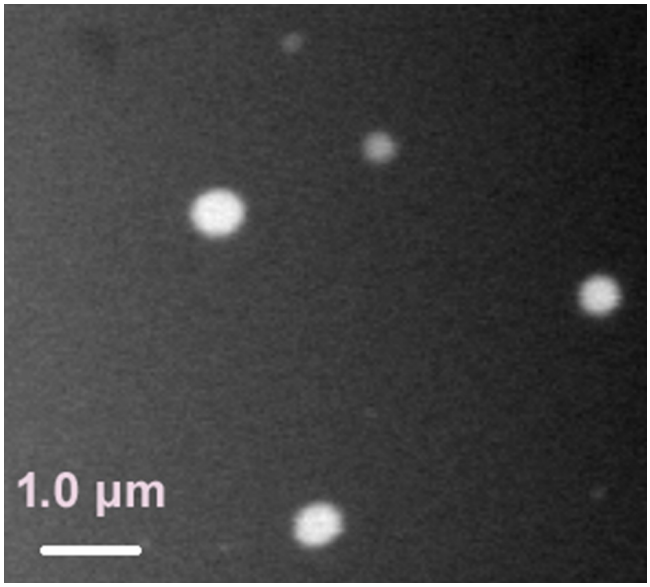

Fig. 1. (Color online) STXM image of nanobubbles at 540 eV. Several nanobubbles (white domains) were found in water (black area).

III. RESULTS AND DISCUSSION

Preparation of the sample was the key step to STXM imaging. As reported by Zhang *et al.* [24], 500 nm water thickness is the top limit for obtaining good results, considering the weak transmission of soft X-ray. Fig. 1 shows a typical STXM image of nanobubbles on the silicon nitride surface in water, with the lateral sizes of the observable nanobubbles being 60–2000 nm.

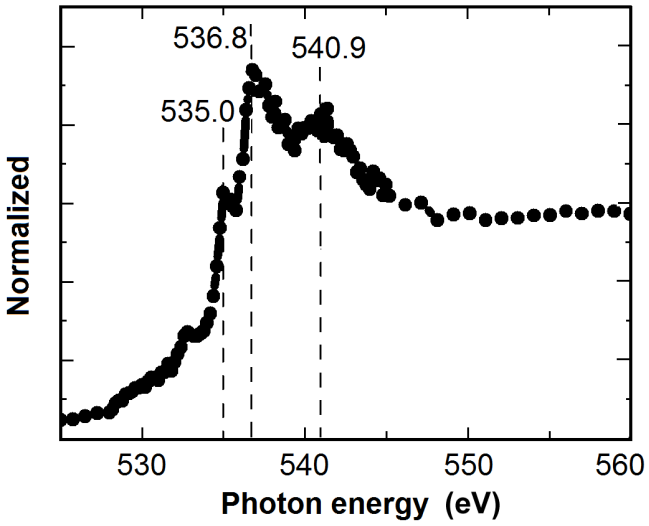

Fig. 2. The spectrum of O K edge extracted from the nanobubbles in Fig. 1.

As shown in Fig. 2, the spectrum of O K edge inside nanobubbles was extracted by deducting the background of water signal. This type of spectrum of O K edge of water has never been reported before. The appearance of three distinct spectral features at 535.0, 536.8 and 540.9 eV implies that there exists a new type of very thin water layers according to the hydrogen bond network analysis. Our results thus clearly indicate that a new phase of water occurs inside the nanobubbles.

IV. CONCLUSION

By using synchrotron based STXM, we found a new water layer structure inside nanobubbles. The three peaks of 535.0, 536.8 and 540.9 eV at O K edge inside the nanobubbles represent novel characteristics of very thin water layers observed for the first time. It strongly indicates that water molecules inside nanobubbles form a new phase of structure. This finding may be essential for explaining the high stability of nanobubble at the water/solid surface and will shed a new insight into the field of molecular water science [25].

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